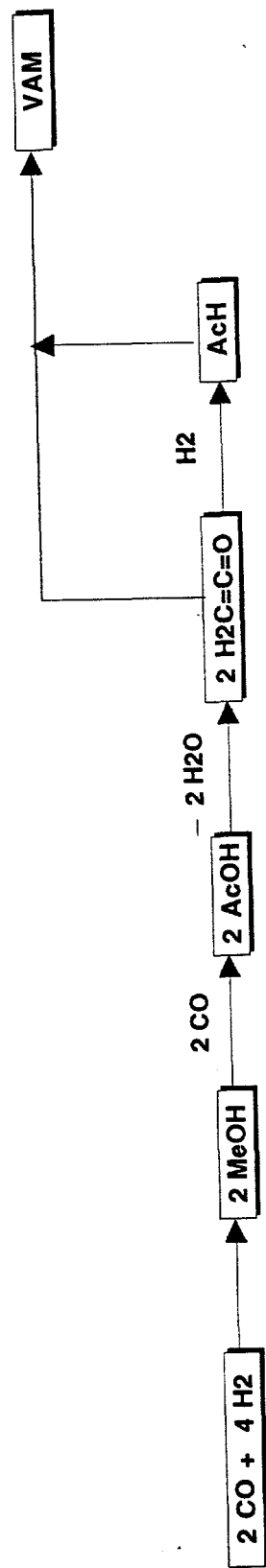


Scheme 1. Conversion of Syngas to VAM via Ketene from Acetic Acid



It is particularly important to point out that this scheme does not have any significant recycle loops. Further, due to the nature of the process, there are numerous opportunities to reduce capital costs through proper integration, and there is a notable economy of scale associated with the size of the intermediate steps.

Consistent with these goals, Eastman has pursued the following tasks in the 4th quarter of 1995:

Task 1.1. Examine hydrogenation of AcOH to acetaldehyde via ketene.

Task 2.1. Examine the direct conversion of AcH and ketene to VAM.

Task 3.1.a. Assess preliminary economics for a process based on ketene hydrogenation.

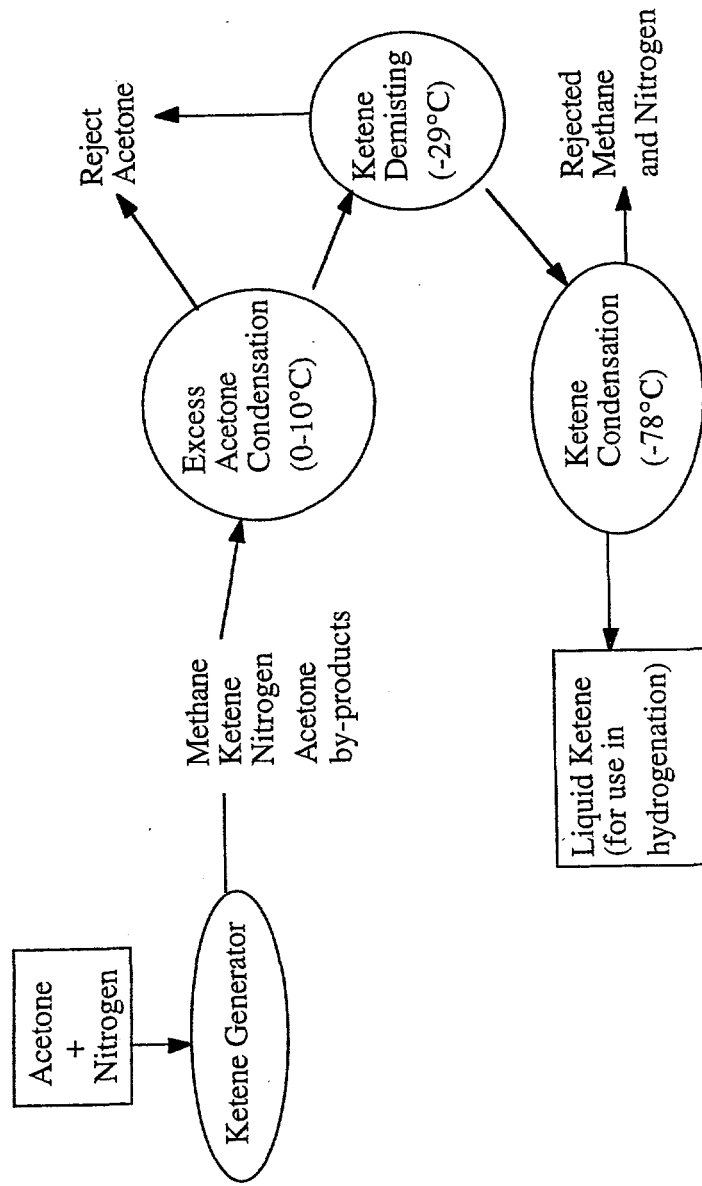
B. Results and Discussion

Task 1.1 Hydrogenation of AcOH via Ketene Intermediates. Over the last several months, Eastman has explored several combinations of different reactor designs for bench-scale production, handling, and hydrogenation of ketene at varying production levels. Ketene can be generated readily from any of four sources, namely, diketene, acetic anhydride, acetic acid, and acetone. Although the preferred method of generating ketene on the commercial scale is via the cracking of acetic acid, a process practiced commercially for more than 70 years, researchers at Eastman are currently using acetone as the source of ketene since the acetone-based processes are easier to operate at the bench scale.

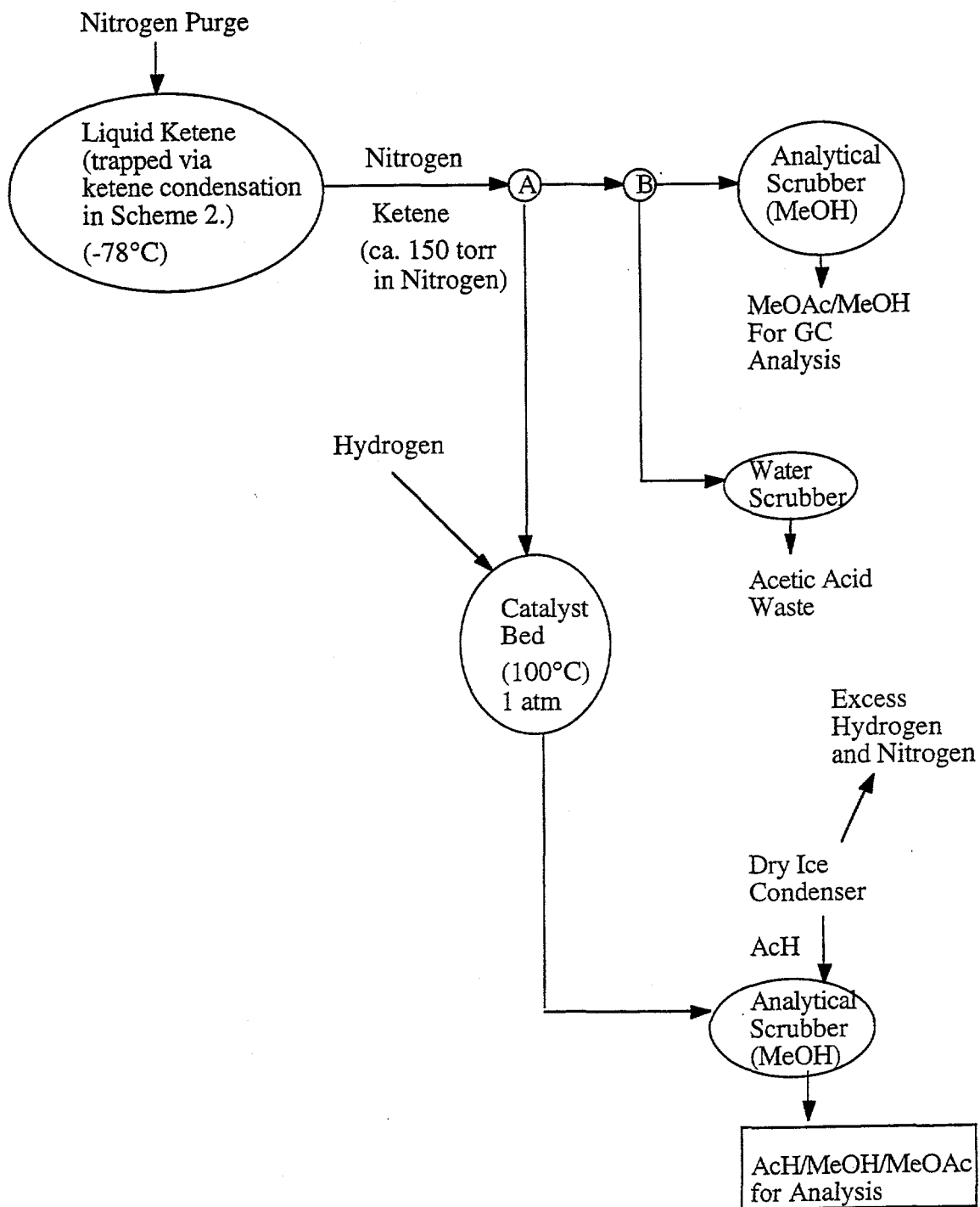
The general method for Eastman's initial studies of the hydrogenation of ketene is represented in the simplified depictions in Schemes 2 and 3; details on the internals, several safety outlets, traps, and a pressure equalizing system for clarity have been omitted. (Scheme 2 represents the generation of ketene from acetone, but a similar apparatus was used for the generation of ketene from acetic anhydride in the earliest work.)

For its initial work, Eastman generated ketene in a separate reactor and stored it temporarily in a dry ice trap. The ketene was then introduced as a gas stream of nitrogen saturated with ketene at -78°C . This produced a gas stream with a ketene partial pressure of about 150 torr (i.e., about 20% ketene in nitrogen). The rate of ketene introduction was first calibrated using a methanol scrubber that quantitatively converts ketene to methyl acetate. The stream was then diverted to the hydrogenation reactor. At the head of the reactor, the ketene stream was mixed with hydrogen (hydrogen/ketene = ca. 2) and introduced into a heterogeneous catalyst bed maintained at steam temperature (100°C) and 1 atmosphere total pressure. The effluent was passed through the same type of analytical scrubber used for calibration, except it was fitted with a dry ice condenser to capture acetaldehyde. Unreacted ketene was again converted to methyl acetate.

Scheme 2. Simplified Schematic of Apparatus for Ketene Generation from Acetone

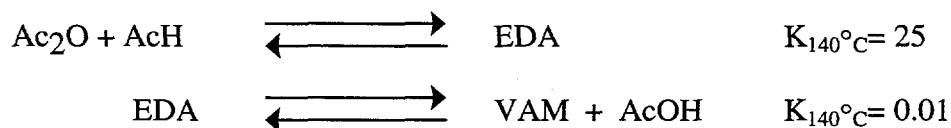


Scheme 3. Description of the Hydrogenation Apparatus

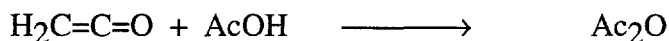


Eastman has examined a number of heterogeneous catalysts using this method. To date, the only catalysts that have shown activity under these conditions are based on Pd, Pt, and Rh. However, Pd has shown much higher rates and selectivities than Pt or Rh, and Eastman has conducted several studies to extend the types of Pd-based catalysts that might prove useful. Results of this study are summarized in Table 3.2.2. In addition, Eastman has conducted a brief, qualitative survey of the effect of time on stream for several of the catalysts (Table 3.2.3) along with a more detailed study of the durability of a Pd sponge catalyst (Figures 3.2.3-3.2.6.) The results to date are excellent for a bench-scale unit. This represents the first direct hydrogenation of ketene to our knowledge, although it has been invoked previously as a likely, but unproven, intermediate in the hydrogenation of acetic acid.

Task 2.1 Direct Conversion of Ketene and Acetaldehyde to VAM. Although methods existed for the conversion of acetaldehyde and syngas-derived acetic anhydride to VAM, Eastman perceived a potential advantage to using the ketene directly for the conversion of acetaldehyde to vinyl acetate. Traditionally, the conversion was carried out by mixing acetic anhydride and acetaldehyde and isolating the vinyl acetate from the equilibrium mixture (represented by the two equations shown below), even though the equilibria favored EDA formation.



Eastman envisioned this addition as a means to consume the AcOH *in situ* by reaction of ketene as follows:



The operating temperatures of this reaction (<140°C) would render it essentially irreversible, and the process should be driven toward the generation of previously disfavored vinyl acetate by the continuous consumption of acetic acid. This process not only has the potential advantage of improving the efficiency of VAM formation, but would replace the acetic anhydride generation facility in earlier concepts with a simplified acetic acid process. (Purity requirements for ketene generation are much less strict than for other acetic acid applications.)

Table 3.2.2 Experimental Results for the Hydrogenation of Ketene to Acetaldehyde

Catalyst	Surface Area m ² /g	Metal Dispersion %	STY, gHAc (1-hr) ⁻¹	STY, gHAc (gPd-hr) ⁻¹	STY, gHAc (gPd-hr) ⁻¹ / Metal Dispersion, %	Ketene Account- ability, %	HAc Selec- tivity, %	Ketene Conver- sion, %
0.5%Pd/Al ₂ O ₃ pellets	238	19.5	188	44.7	2.29	84	72	59
5% Pd/BaSO ₄	4.2	2.6	1416	25.4	9.77	70	70	78
5% Pd/CaCO ₃ w/Pb	6.42	2.9	736	17.6	6.07	56	43	77
5% Pd/CaCO ₃	13.99	10.7	1151	32.1	3	79	74	82
5% Pd/BaCO ₃	5.21	2.9	1392	25.1	8.66	81	72	67
5 % Pd/C	1259	25.1	713	37.1	1.48	78	76	92
0.5%Pd/Al ₂ O ₃ powder	103	17.1	1639	31.3	1.83	82	77	77
1% Pd/TiO ₂	9	1.7	108	15.8	9.29	88	68	36
3% Pd/SiO ₂	55	14.4	400	33.3	2.31	83	79	80
*5% Pd/BaCO ₃	5.21	2.9	559	9.3	3.21	83	54	37
Pd Sponge	0.13	0.004	1180	0.47	117.5	91	66	27

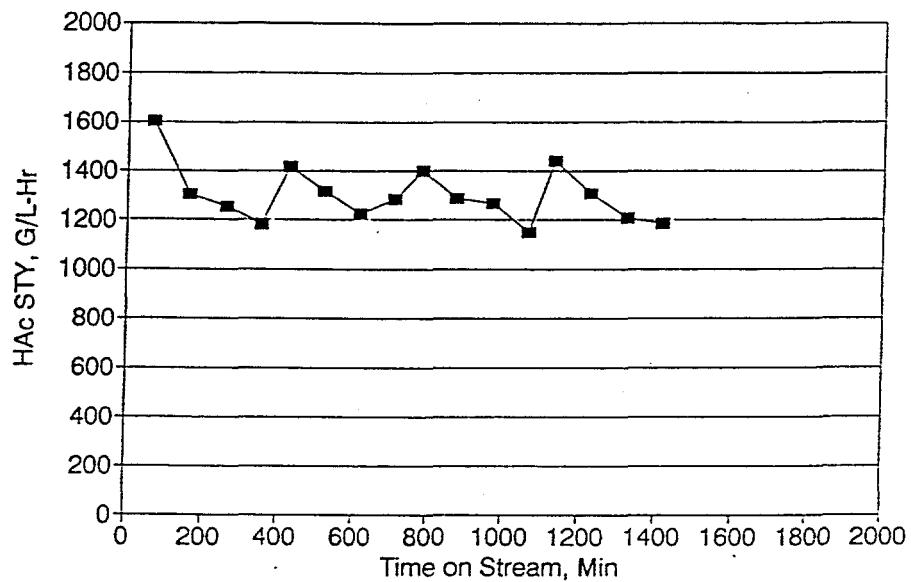
Data presented is from the performance of the fourth sample.

All reactions were run in a fixed catalyst bed, steam-heated reactor except for *ed Pd/Ba₂CO₃ run which was run in slurry phase reactor.

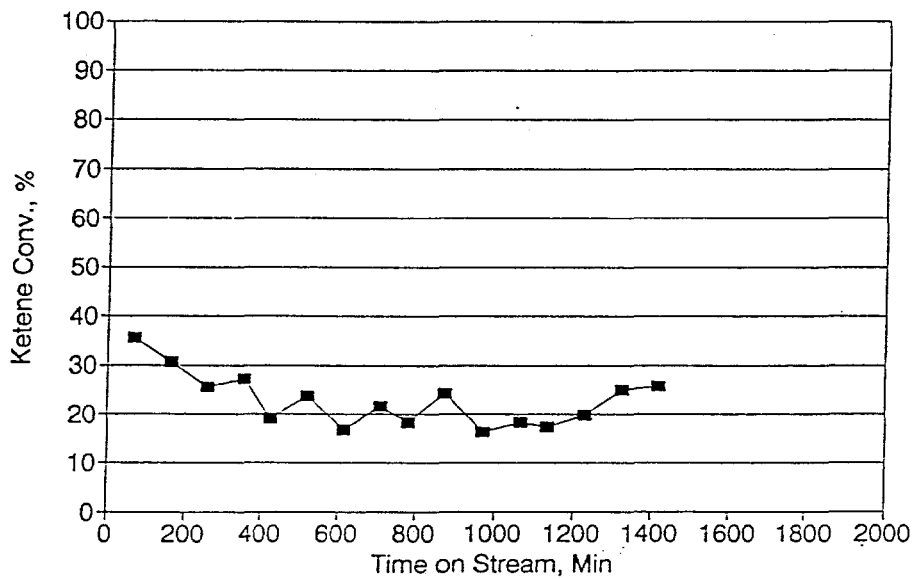
Table 3.2.3 Percent Change in Performance Between 4th and 16th Sample

Ref No. X24668	Catalyst	Rate	Ketene Accountability	HAc Selectivity	Ketene Conversion
014	0.5%Pd/Al ₂ O ₃ pellets	-32	-2	-14	-22
033	5% Pd/BaSO ₄	-3	+7	-7	-8
038	5% Pd/CaCO ₃ w/Pb	-18	+16	+2	-19
043	5% Pd/CaCO ₃	-6	-28	-23	+23
048	5% Pd/BaCO ₃	-11	+6	+6	-16
085	5 % Pd/C	-16	+14	+11	-24
060	0.5%Pd/Al ₂ O ₃ powder	-41	-33	-43	+4
066	1% Pd/TiO ₂	+1	-14	-25	+33
072	3% Pd/SiO ₂	-14	+10	+8	-20
058	5% Pd/BaCO ₃	slurry phase			
077	Pd Sponge	+0.4	+1	+6	-4

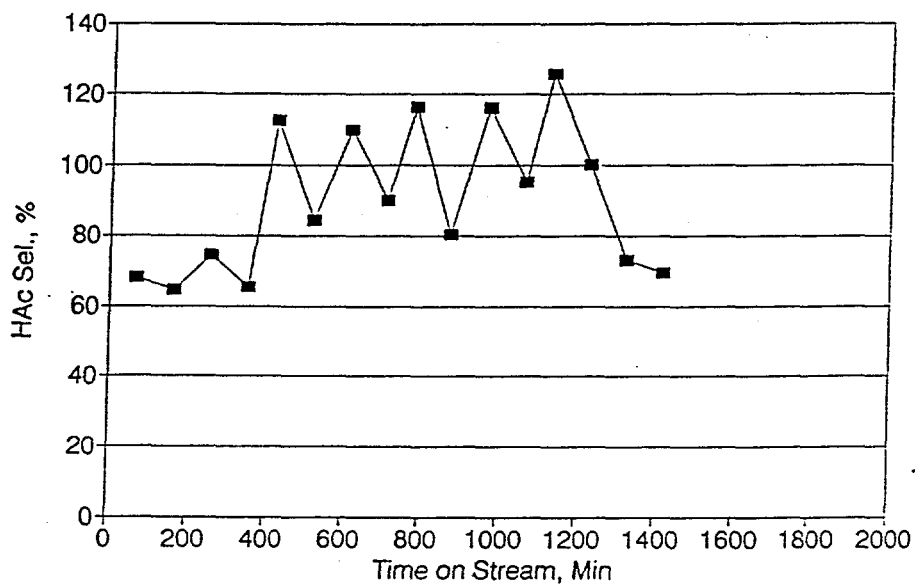
**Figure 3.2.3 HAc STY vs Time On Stream
Pd Sponge**



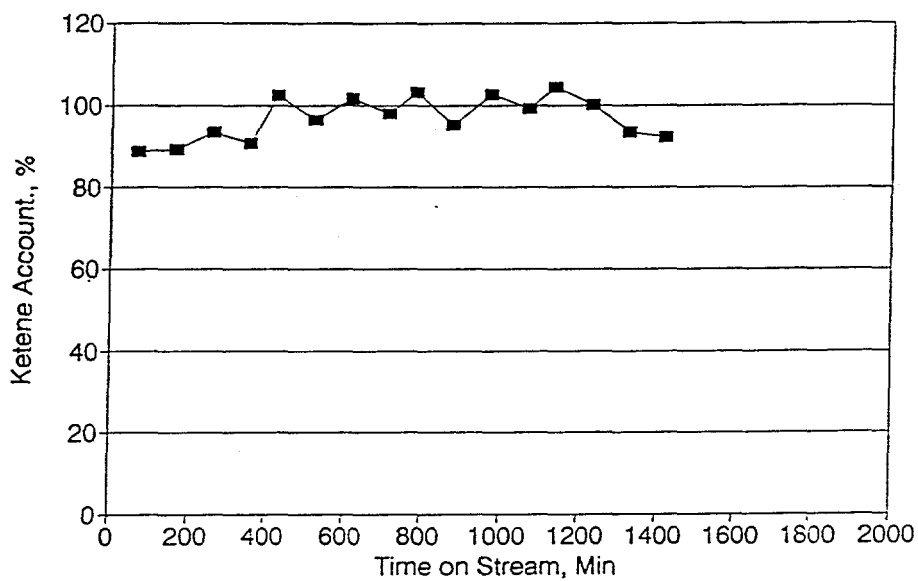
**Figure 3.2.4 Ketene Conversion vs Time On Stream
Pd Sponge**



**Figure 3.2.5 HAC Selectivity vs Time On Stream
Pd Sponge**



**Figure 3.2.6 Ketene Accountability vs Time On Stream
Pd Sponge**



Over the last quarter, Eastman has realized this advance in VAM generation. Using a gas-stripped reactor such as the one diagrammed in Scheme 4, Eastman has demonstrated a bench-scale unit for the continuous conversion of acetaldehyde and ketene to VAM. Operationally, ketene generation and introduction was identical to that used in hydrogenation experiments, and acetaldehyde was also introduced as an approximately 20% AcH vapor by bubbling nitrogen through a column of acetaldehyde maintained at -20°C . After combination of the ketene and acetaldehyde streams with a small stream of nitrogen, the mixture is fed to the reactor in Scheme 4. (The final feed composition is 6% ketene, 8% AcH, and 86% nitrogen.) The utilization of a gas-stripped reactor is important since this allows Eastman to strip VAM from the solution before VAM can undergo further reactions. Operating conditions and results of an early one week run, where several conditions were varied as we learned how to operate the system, are summarized below:

Starting solution:

29.4 g starting mass
250 mmoles Ac_2O
27 mmoles HOAc
2.8 mmoles $\text{PhSO}_3\text{H}\cdot\text{H}_2\text{O}$ (benzenesulfonic acid monohydrate),
later increased to 13.1 mmoles

Conditions:

operated for a total of 28.25 hours over a 5 day period
total ketene and acetaldehyde added over this period:
1187 mmoles ketene
1695 mmoles acetaldehyde
steam heat at 98°C or electric heat at 150°C
most of the volatile product (HAc, Ac_2O , vinyl acetate) isolated from
the dry ice trap: *no HOAc found in the dry ice trap!*

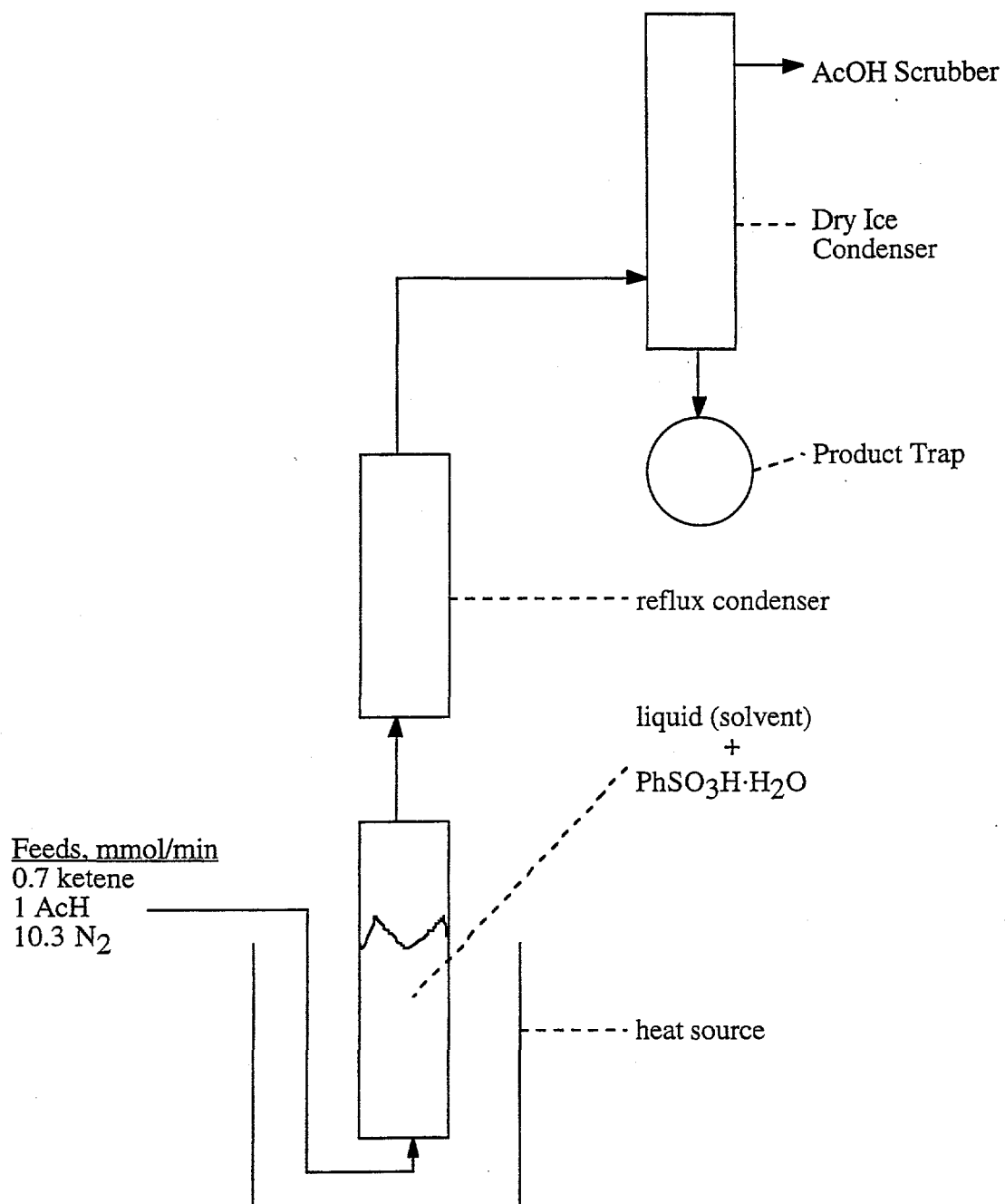
Contents of heel solution after reaction:

33.2 g recovered
6 mmoles HOAc
180 mmoles Ac_2O
72 mmoles EDA

Yield data:

total vinyl acetate (VAM generated/ketene fed X 100%) yield = 59%
total ketene accountability = 84%
total acetaldehyde accountability = 103%

Scheme 4. Gas Stripped Reactor for Direct Conversion of Ketene and Acetaldehyde to Vinyl Acetate



As can be seen from Table 3.2.4, key variables in this operation are the catalyst levels and operating temperatures. Initial studies using N-methyl pyrrolidinone (NMP, a cyclic tertiary amide) as the solvent rather than a mixture of acetic acid and acetic anhydride gave similar results.

Table 3.2.4. Effect of Catalyst Level and Temperature on VAM yields in the Gas-Stripped Reactor.

<u>mmol PhSO₃H.H₂O</u>	<u>temp., °C</u>	<u>yield vinyl acetate, %*</u>
2.8	150	21
13.1	150	78
13.1	98	37
13.1	150	80

*yields = VAM obtained/ketene fed X 100%. These yields do not account for unreacted ketene and represent single pass yields.

As we have learned to operate this system and better close material balances, the vinyl acetate yields have steadily improved, and yields (as calculated above) are now in excess of 90%. (The optimization studies are still underway and will be reported in more detail in the next quarterly report.) Further, although it does not significantly affect the design and operation of the unit, early observations indicate that, contrary to Eastman's original concept, the Bronsted acid catalyzed addition of ketene to acetaldehyde *may* actually proceed via a direct esterification of acetaldehyde to VAM without forming EDA as an intermediate.

Task 3.1.a. Preliminary Economics for a Ketene Based Process. Having identified operable processes at the bench scale for both the hydrogenation of ketene and the direct esterification of acetaldehyde with ketene, Eastman now has sufficient information to undertake *preliminary* economic estimates for the overall process. The conceptual flowsheet is in place. Eastman already has estimates for an appropriately sized acetic acid plant and ketene furnace, although the models will require some updating. Further, designs for the conversion of acetaldehyde and ketene to VAM are well underway. Preliminary estimates will *not* account for the available synergies between the components of the facility and will purposely be conservative.

C. Future Directions

General. Over the last quarter, Eastman has completed the construction of two additional ketene generation systems and has modified its existing reactor to allow faster, more reproducible, ketene introduction rates in both the hydrogenation and VAM generation processes. One is now operational and the second is currently being checked out. Additional efforts are being directed toward obtaining better, more reproducible methods for determining ketene levels. This is particularly critical since the largest variable in determining the efficiency of these reactions is the variability in measurements to obtain ketene balances.

Task 1.1 Hydrogenation of Ketene. Over the next quarter Eastman will be:

- a) pursuing a detailed study of the Pd catalysts, particularly in the presence of lower levels of diluent. (The goal is to approach the likely conditions in a plant environment.)
- b) examining homogeneous catalysts and reactor designs for this hydrogenation.

Task 2.1 Conversion of Acetaldehyde and Ketene to VAM. Over the next quarter, Eastman expects to:

- a) Continue its investigation of gas-stripped reactors and alternative designs for conducting these reactions.
- b) Examine heterogeneous catalysts.
- c) begin integrating the process with the ketene hydrogenation. (This will include an examination of a speculative direct conversion of ketene to vinyl acetate wherein the hydrogenation will be conducted in the presence of an acid catalyst.)

Task 3.1.a Preliminary Economics. Eastman expects to complete a *preliminary* estimate by the end of the second quarter of FY1996.

D. Summary

Over the last quarter Eastman has demonstrated that they could readily hydrogenate ketene to acetaldehyde, a reaction heretofore unknown. Eastman has also demonstrated that acetaldehyde could subsequently be recombined with ketene to generate VAM without the requirement for a separate acetic anhydride generation and reaction step. These form a very simple overall process for the generation of VAM. Eastman will optimize these processes over the next several months and will be generating initial cost estimates for the production of VAM from syngas by this method.

Task 3.3 New Processes for Alcohols and Oxygenated Fuel Additives

3.3.1 Isobutanol Synthesis in a Three Phase System (RWTH Aachen)

Fixed Bed Reactor Design and Runs

The optimal reaction conditions with ZrO₂/ZnO/MnO catalysts are presented below.

Overall conditions were as follows:

Catalyst:	ZrO ₂ /ZnO/MnO/K/Pd (pH 9)
GHSV:	23000 h ⁻¹
Reactor:	Fixed Bed

The data have been summarized from 40 on-line measurements.

The mechanical stress of changes in pressure is much greater than that with changes in temperature, which leads to an increase in deactivation during pressure programming. This fact is borne out by the values at 25 MPa which were measured initially.

Figures 3.3.1 and 3.3.2 clarify that high pressures promote activities toward isobutanol and methanol production. The influence of temperature increases with increasing pressure. Increasing temperature itself decreases the yield of isobutanol and methanol. CO conversion increases nearly linearly with temperature and pressure (Figure 3.3.3). Selectivity to CO₂ is not affected by pressure, but increases rapidly with higher temperatures (Figure 3.3.4).

Figure 3.3.1 STY to Isobutanol vs Temperature and Pressure

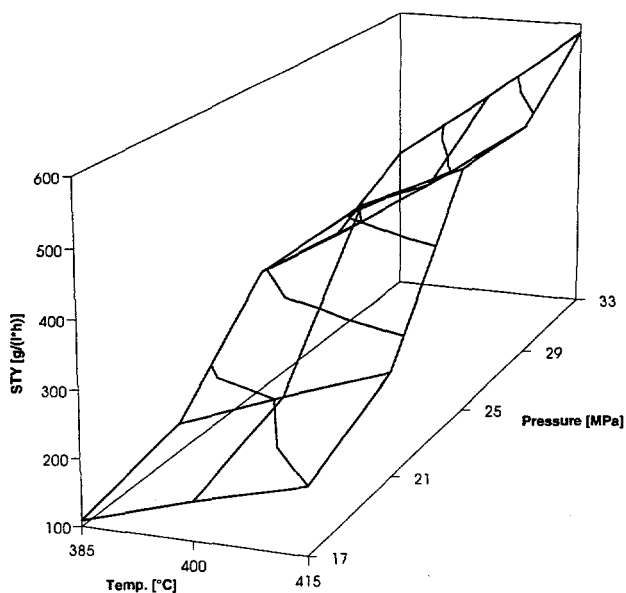


Figure 3.3.2 STY to Methanol vs Temperature and Pressure

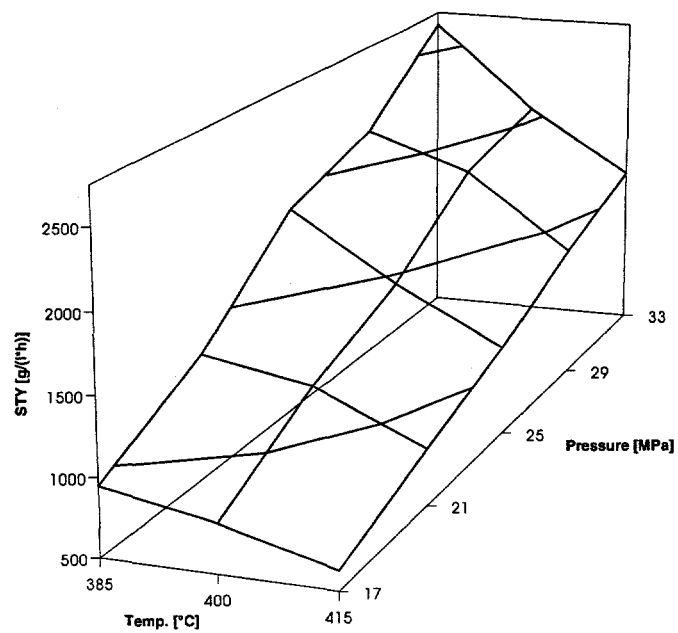


Figure 3.3.3 CO Conversion vs Temperature and Pressure

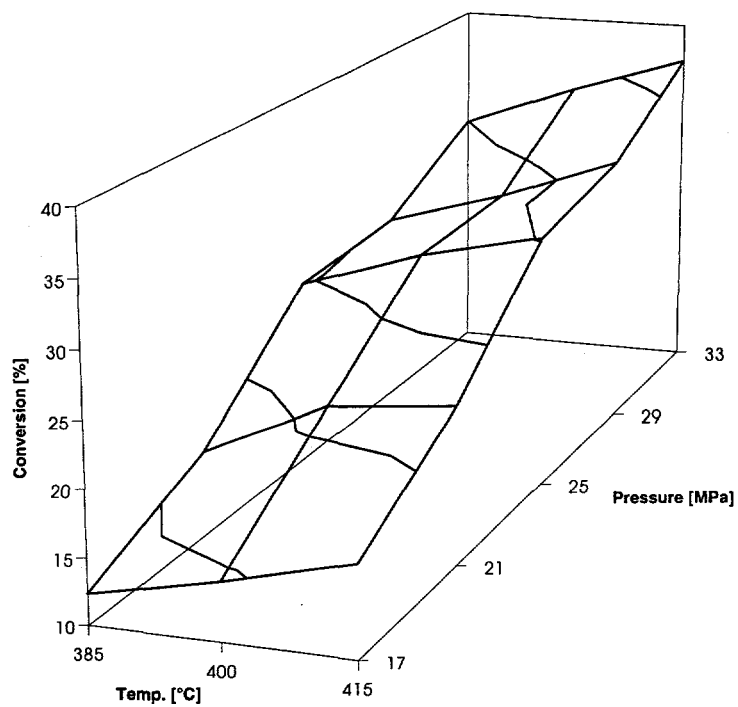
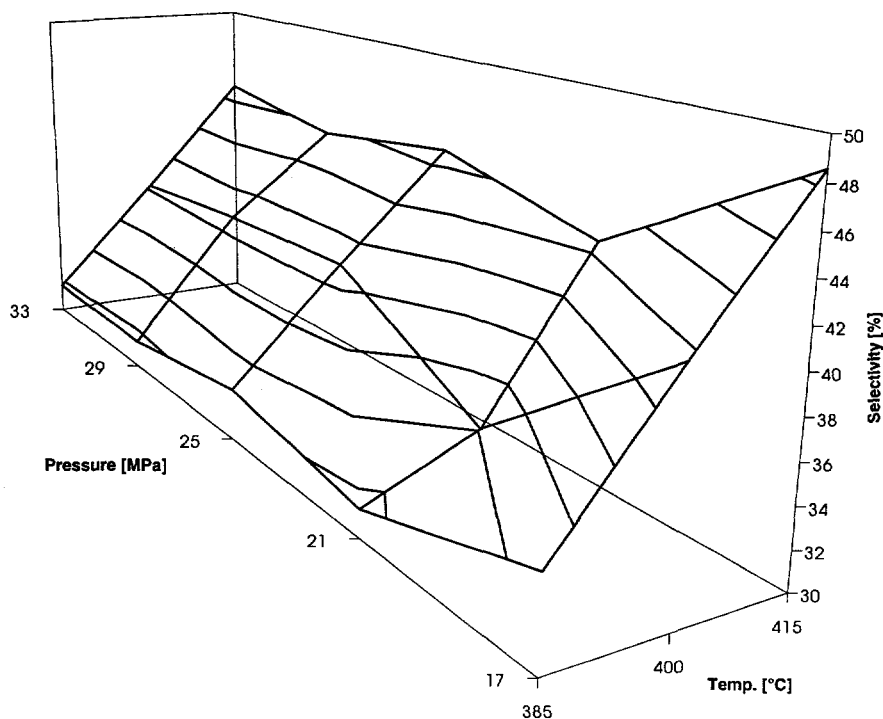


Figure 3.3.4 Selectivity to CO₂ vs. Temperature and Pressure



Slurry Reactor Design and Runs

Design

Over the last quarter, significant progress concerning the slurry reactor has been achieved. This progress concerns the theoretical estimation of the fundamental mass transfer coefficients as well as the results from runs.

It is well known that three limiting steps regarding methanol synthesis in a slurry system can exist¹

1. mass transfer from the bulk gas phase to the bulk liquid
2. mass transfer from the bulk liquid to the boundary layer of the catalyst particle
3. reaction including pore diffusion to the active sites.

Concerning these steps in the isobutanol slurry system the following can be said:

1. The mass transfer coefficients k_{1a1} for the step from the bulk gas to the bulk liquid phase were estimated with a correlation examined by Yagi and Yoshida². For hydrogen and carbon monoxide, k_{1a1} coefficients are in the range from 0.7 to 3.3 s⁻¹. These values are

¹N. H. Sweed: *Intraparticle and interphase transport resistances in gas-liquid-solid catalytic reactors*. In: A. E. Rodrigues, J. M. Calo, N. H. Sweed/W. Kotowski, J. Kliniec, Z. Kasprovicz: Int. Congress CHISA, Praha, Sept. 1984, S.1.

²H. Yagi, F. Yoshida: *Gas Absorption by Newtonian and Non-Newtonian Fluid in Sparged Agitated Vessels*, Ind. Eng. Chem. Proc. Des. Dev. 14, 488 (1975).

- a little higher for methanol synthesis due to the low surface tension of decalin³. Based on these values, a mass transfer limitation at this step is unlikely.
2. The volumetric mass transfer coefficient $k_s a_s$ for step 2 in the isobutanol slurry system is between 30 and 300 s^{-1} , depending on component and particle size. These values of $k_s a_s$ are 1-3 orders of magnitude higher than the coefficients $k_l a_l$ for step 1. Thus, the mass transfer from the bulk liquid to the boundary layer of the catalyst particle as a limiting step can be ignored.
 3. Assuming an isothermal catalyst particle, it is unlikely that step 3 will be rate-controlling for a catalyst particle smaller than 0.2 mm in the slurry bed (compared to a catalyst particle of 1 mm in diameter in a fixed bed reactor). The catalyst particles used in the slurry reactor were always crushed smaller than 0.2 mm.

To prove the mathematical correlations, a run using the CSTR containing no inert oil was conducted. After eight on-line measurements, decalin was added using a high-pressure pump directly into the reactor up to the level of normal slurry runs. Subsequently, a second set of eight measurements was started. The results with and without decalin were nearly identical. This leads to the conclusion that synthesis is not affected by decalin at normal reaction conditions.

Runs: Comparison of CSTR to Fixed Bed Reactor

Measurement of actual catalyst activities with the slurry reactor was possible only by installing a preheater upstream of the slurry reactor. The preheater was filled with 10.5 ml glass particles and heated to 400°C. This arrangement seemed to cause adsorption of catalyst poisons at the surface of the glass particles instead on the active site of the catalysts. The effect was the same as seen in the fixed bed runs.

As shown in Table 3.3.1, STYs towards alcohols are quite similar but more methanol is produced in the slurry reactor. This might be an effect of temperature (see quarterly report 02/95).

Table 3.3.1 Comparison Of Results In Two Different Reactors At Similar Reaction Conditions

	slurry reactor	fixed bed reactor
STY isobutanol [g/(l*h)]	204	370
STY methanol [g/(l*h)]	1057	738
isobutanol/methanol	~ 0.19	~ 0.50
Conversion CO [%]	23	37
Selectivity CO2 [%]	54	57
GHSV [h ⁻¹]	16900	17600

Temperature: 415°C, Pressure: 25 MPa, Catalyst: BASF-ZnO/Cr2O3/K

³S. Ledakowicz, H. Nettelhoff, W.-D. Deckwer: *Gas-liquid mass transfer in a stirred autoclave reactor*. In: Ind. Eng. Chem. Fundam., Bd. 23, 1984, S. 510/S. A. Miller, A. Ekstrom: *Solubility and mass-transfer coefficients for hydrogen and carbon monoxide in n-octacosane*. In: J. Chem. Eng. Data, Bd. 35, 1990, S. 125.

Solvent

Following a publication by Kotowski et al., undecanol has been tested to obtain an alternative for decalin⁴. Undecanol was not found to be stable.

Catalyst Screening

To supplement the description of the second isobutanol unit in the last quarterly report, additional details are given here. The oven has been equipped with a small ventilator for minimizing the gradient of temperature. The cooling system used in this unit is composed of one condenser (1.2 meters) cooled to temperatures < -30°C and two cooling traps cooled to temperatures of -78°C. With this system, condensation of nearly the total product amount is possible.

As in "Isobutanol Unit I," gas samples are collected and analyzed quantitatively. The first catalytic tests have been performed successfully and the first alkaline impregnated catalysts have been screened (see report 02/95).

Test Routine for Catalyst Screening

The first information that should be presented here is a suitable and comparable test routine. The difficulties with this are the strong variations in weight and volume of different catalysts. Therefore the catalyst screening will be constant in GHSV and all STYs will be given in g/kg[cat]·h⁻¹. Additionally, all important data for catalyst comparison are collected. Reduction is performed as follows:

Gas: H₂
Pressure: 30 bar
GHSV: 10000 h⁻¹
Temperature: rising from 20 to 350°C
Heating rate: 4°/min

After 350°C is reached, the reaction medium is changed from hydrogen to syngas:

Gas: CO/H₂=1
Pressure: 250 bar
GHSV: 20000 h⁻¹
Temperature: 2 or 3 setpoints between 385 and 430°C
Heating rate: 4°/min

Before sampling, the catalyst is allowed to come to steady state at each setpoint (>1 h). This modified reduction procedure has been chosen to save time in the test routine. In addition, contact of the catalyst with syngas between 200 and 350°C is avoided. A comparison of the two different reduction procedures will be reported later.

⁴W. Kotowski, S. Ledakowicz, R. Zarzycki, L. Nowicki, H. Berndt: *Methanol-Synthese an einem suspendierten CuO-ZnO-Mn₂O₃-Katalysator-Kopplung der Erzeugung von Methanol und Energie*. Chem-Ing.-Tech. 67 (1995) Nr. 1, S. 80-82.

Results

In the last quarterly report the section "Alkaline Free Catalysts" dealt with ZrO₂/ZnO/MnO type catalysts washed free of alkaline metals. The intention is impregnation of these catalysts with alkaline and/or transition metals in order to obtain information about the influence of these components. The first members of this catalyst type have now been tested, and the main data are presented in Table 3.3.2.

Table 3.3.2 Screening Results

Run-Nr. Catalyst	BJ 1.1 BJ 27/25)	BJ 1.2 BJ 27/25)	BJ 2.1 BJ 36(K6)	BJ 2.3 BJ 36(K6)	BJ 4.1 BJ 36/3% K7)	BJ 4.2 BJ 36/3% K7)
Volume /ml1)	4.0	4.0	3.1	3.1	3.9	3.9
Mass /g1)	5.3	5.3	4.0	4.0	5.3	5.3
Temp. /°C	385	405	385	415	385	415
S [MeOH] /% 2)	70	48	88	61	72	50
S [i-BuOH] /% 2)	14	18	7	13	3	7
STY [MeOH]	630	396	851	467	323	346
STY [i-BuOH]	125	150	66	101	13	52
STY [alcohols] 3)	800	600	944	603	344	425
STY [products] 4)	900	818	965	762	447	700

1) values belonging to the catalyst

2) selectivity concerning organic liquids

3) all detectable alcohols

4) total liquid product amount excluding water

5) ZrO₂/ZnO/MnO/K (pH9)

6) ZrO₂/ZnO/MnO (pH11) alkaline free

7) ZrO₂/ZnO/MnO (pH11) + 3% K₂O

Catalyst BJ 27/2 was precipitated from metal nitrates at pH 9, as described earlier. BJ 36 was made by coprecipitation at pH 11 using the same procedure, but was washed alkaline free. Table 3.3.2 shows no tendencies, but does show remarkable changes in activity and selectivity related to the amount of potassium. A fourth catalyst (BJ 36 with 1% K), which could not be included in the table, showed total STYs below 250 g/kg[cat]·h⁻¹ derived mainly from methanol and some isobutanol. With testing, the entire set of catalysts tendencies might become clear.

Catalyst Preparation

Among the currently used strategies to elucidate the scope of the Zr/Zn/Mn-oxide system, the use of different synthesis methods was envisaged. For this purpose the following preparation methods were chosen:

- Coprecipitation
- Complexation
- Sol-Gel Methods
- Impregnation

In this quarter synthesis was mainly concentrated on the use of impregnation techniques and the optimization of sol-gel methods for our system.

Sol-Gel Based Catalysts

As described earlier (report 02/95, 03/95), the sol-gel method involves the formation of an inorganic oxide network by controlled hydrolysis of suited metal precursors. The objective of this study is to develop synthesis methods that lead to homogeneous distributions of zirconia, zinc and manganese oxides. This is done by introducing zinc and manganese salts during the polymerization of zirconium alkoxides. With the proper use of stabilizing agents, the polymerization reactions can be adjusted in order to obtain homogeneous, clear gels. Control of hydrolysis and condensation reaction rates can be influenced by the addition of complexing agents such as acetic acid or acetyl acetone. In addition one can differentiate between acid and base catalyzed sol-gel reactions. Under acidic conditions, hydrolysis occurs at a faster rate than does condensation, and the resulting gel is weakly branched. Condensation is accelerated relative to hydrolysis with increasing pH. Thus, a base-catalyzed gel is highly branched and contains colloidal aggregates. In this way the pore structure (surface area, pore volume and pore size distribution) can be adjusted. The results are provided in Tables 3.3.3-3.3.5.

Table 3.3.3 Influence Of Acetic Acid On Zr/Zn/Mn-Gels¹

HOAc/Zr	H ₂ O/Zr	Gel Time ²	Morphology
1	10	immediate	Precipitate
1.5	10	immediate	Gel/Precipitate
1.75	10	2 min. 30 sec.	Gel/Precipitate
2	10	19 days	Gel
4	10	4 months	Gel

¹General Procedure: Zirconium propylate (100 mmol, 70 wt% solution in n-propanol) was stirred with the appropriate amount of acetic acid for 60 minutes. Zinc and manganese nitrate (each 100 mmol) were dissolved in 85 ml n-propanol and added instantaneously.

²Gel Time is defined as the time elapsed between mixing the reagents and the formation of a gel so that no vortex can be produced by the stirrer.

Table 3.3.4 Influence Of Nitric Acid On Zr/Zn/Mn-Gels¹

HNO ₃ /Zr	H ₂ O/Zr	Gel Time	Morphology
1.33	10	28 sec.	Gel
1.56	10	13 min. 25 sec.	Gel
1.78	10	10 hours	Gel

¹General Procedure: Zirconium propylate (100 mmol, 70 wt% solution in n-propanol) was stirred with the appropriate amount of nitric acid for 60 minutes. Zinc and manganese nitrate (each 100 mmol) were dissolved in 85 ml n-propanol and added instantaneously.

Table 3.3.5 Influence Of Acetylacetone On Zr/Zn/Mn-Gels¹

HNO ₃ /Zr	acac/Zr	H ₂ O/Zr	Gel Time	Morphology
0	0.25	10	immediate	Precipitate
1.11	0.25	10	25 sec..	Gel/Precipitate
1.33	0.25	10	30 min.	Gel/Precipitate
1.56	0.25	10	11 days	Gel

¹General Procedure: Zirconium propylate (100 mmol, 70 wt% solution in n-propanol) was stirred with the appropriate amount of nitric acid and acetylacetone for 60 minutes. Zinc and manganese nitrate (each 100 mmol) were dissolved in 85 ml n-propanol and added instantaneously.

The data clearly show the influence of the stabilizing agents on gel time and morphology. In some cases initially a clear gel is obtained, which becomes cloudy after several hours. This is caused by prolonged condensation processes with aging. The wet gels were transformed into aerogels via supercritical drying in an autoclave. Analyses obtained so far indicate that this method leads to formation of mesoporous materials with surface areas ranging from 80-130 m²/g. XRD analysis indicated the formation of crystalline zinc oxide. In a separate experiment (Table 3.3.6), it was found that this phase is formed during the supercritical drying step.

The influence of the supercritical drying step and the manner of addition of the zinc and manganese salts were tested with acetic acid as the stabilizing agent (Table 3.3.6). In the above described experiments, the water needed for gel formation was introduced as the crystal water contained in the metal salts. The influence of the metal salts upon gel formation was investigated by producing a gel first and mixing it with the metal salts afterward, followed by a supercritical drying step. The BET data show that the latter method leads to a compound that has a slightly smaller surface area (101 vs. 113 m²/g); however, the pore size is larger (70 vs. 55 Å). The influence of the drying step becomes evident by comparing an ordinarily dried gel with a supercritically dried one. The xerogel produced has a very low surface area, and it appears that supercritical drying is needed to obtain large surface areas.

Table 3.3.6 Influence of Post Treatment and Introduction of Metal Precursors

HOAc/Zr	H ₂ O/Zr	Gel Time	Post Treatment ¹	BET (m ² /g)	Mean pore size (Å)
1.75	10	2 min. 30 sec.	xerogel	17	40
1.75	10	2 min. 30 sec.	aerogel	113	55
1.75	4+10	1 min.	aerogel	101	70

¹The xerogel was dried by evaporating the solvent in a rotavap. Subsequently the powder was dried in an oven at 120°C for 16 hrs. The aerogel was prepared as follows: after dispersing the gel with n-propanol (200 ml), the autoclave was flushed with nitrogen and pressurized with 50 bar nitrogen. Then the autoclave was heated to 280°C (1°C/min.). After keeping this conditions (280 °C, ca. 140 bar) constant for 30 minutes, the autoclave was vented slowly (ca. 1 bar /min.). In all cases the powders obtained were calcined at 400°C.